

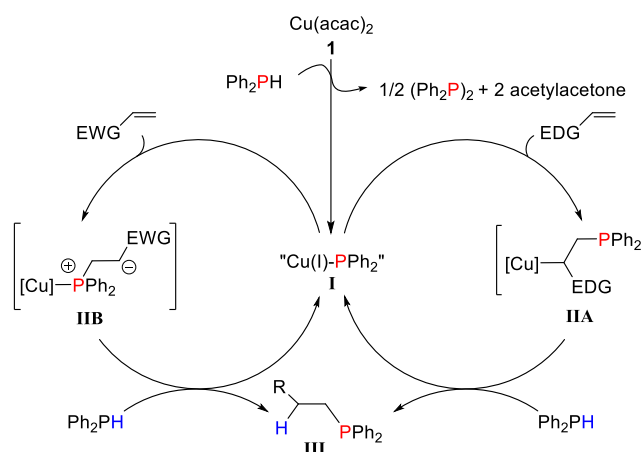
Advances in Photocatalytic Hydrophosphination

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An important challenge for chemists is increasingly efficient routes to element–carbon bonds, as characterized by energetic costs and atom economy, among other factors. An atom-economical route for element–carbon bond formation is the metal-catalyzed addition of an E–H bond across an unsaturated substrate, generally termed heterofunctionalization. For hydrophosphination or P–C bond formation, challenges in substrate scope, selectivity, and catalyst have loomed.¹ Many catalysts are known,² and a rich variety of mechanisms have been uncovered in these reactions.³ Starting from poor initial hydrophosphination catalysis with zirconium compounds, a family of earth abundant, highly active, and selective catalysts have been discovered and investigated, and photocatalysis is critical to this activity.

Simple copper catalysts that may be the most active known but are certainly the most synthetically accessible.⁵ Under visible or UV photolysis, Cu(acac)₂ is highly active for the hydrophosphination a range of phosphine and unsaturated substrates. These reactions are on a scale of minutes to hours, allowing for broad testing of hydrophosphination with a wide variety of substrates, making this the go-to catalyst for synthetic screening. The mechanism of this catalysis diverges based on substrate. After a common reduction step with sacrificial phosphine substrate, the active copper(I) catalyst can either undergo an insertion-based mechanism of the phosphido ligand can attack an electron poor alkene. Spectroscopic and computational analysis point to a LUMO with significant Cu–P σ* character. This would indicate that photocatalysis for early and late metals are similar and therefore may extend to other π-basic ligands. Analysis of mechanism with respect to expanding the substrate scope of hydrophosphination and addressing related challenges will be detailed.



1) Bange, C. A.; Waterman, R. *Chem. Eur. J.* **2016**, 22, 12598. 2) Novas, B. T.; Waterman, R. *ChemCatChem* **2022**, 14, e202200988. 3) Rosenberg, L. *ACS Catal.* **2013**, 3, 2845. 4) Dannenberg, S. G.; Waterman, R. *Chem. Commun.* **2020**, 56, 14219. 5) Dannenberg, S. G.; Seth, Jr., D. M.; Finfer, E. J.; Waterman, R. *ACS Catal.* **2022** accepted.